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COLE-COLE DIAGRAM AND THE DISTRIBUTION OF RELAXATION TIMES

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ABSTRACT

The completeness of the Cole-Cole diagram in the analysis of dielectric relaxation is proved by showing explicitly that a semicircle in the Cole-Cole diagram corresponds uniquely to a Debye relaxation function. A method is established to distinguish a continuous distribution of relaxation times from a single relaxation time.

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I. INTRODUCTION

In the frequency domain, the relaxation function is a complex function of the frequency, the real component is called the dispersion and the imaginary component the absorption. In the analysis of the dielectric relaxation in the frequency domain, a very convenient representation, in terms of the Argand diagram of the complex plane of the relaxation function, was introduced by Cole and Cole.[1] The usefulness of this representation is found also in the analysis of other kinds of relaxations, such as that of viscoelastics,[2] paramagnetics,[3] plasmas and semiconductors.[4] In spite of this universality, the mathematical foundation of this representation does not seem to have been established until recently.[5]

While the approach of Ref. 5 is of a very general and formal nature, in the present paper, we will treat a special, but physically a better understood case: a system of relaxation which obeys linear kinetics, such as Debye relaxation in dielectrics,[6] Casimir and Du Pre relaxation in paramagnetics,[3] and Lorentz relaxation in plasma.[7] For such a system, the Argand diagram shows a semicircle. The mathematical proof of this conclusion is of a simple algebraic nature and can be found in the literature.[8] But this constitutes only a proof of the sufficient condition. In part II of the present paper, we would like to prove the necessary condition. Therefore, we establish the completeness of the semicircle in the Argand diagram representation. We will use the familiar symbols of dielectric relaxation, in accordance with the title of our paper, but a general implication is obvious.

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Because of the method of proof we introduced in the preceeding problem, we can establish a criterion to distinguish whether a relaxation function has a single relaxation time, or a continuous distribution of relaxation times. This we will discuss in Part III.

II. COMPLETENESS OF THE COLE-COLE DIAGRAM

Elsewhere[5] we have proved, based on an invariance of the Kronig-Kramers relation, that: an Argand diagram (or the equivalent Cole-Cole diagram in the dielectrics) determines completely, up to an undeterminable scale factor, the relaxation function. In the present work, we will prove explicitly that a semicircle in the Cole-Cole diagram uniquely implies that the relaxation function is that of Debye.

We start from the following equation,

$$\epsilon^*(\omega) = \epsilon_\infty + (\epsilon_0 - \epsilon_\infty) \int_0^\infty \frac{g(\tau)}{1 + i\omega\tau}\, d\tau, \tag{1}$$

where $g(\tau)$ is a distribution function of the relaxation time τ, and the other symbols have the usual meaning.

We will use the following reality conditions:

1. $g(\tau) > 0$,

2. $\int_0^\infty g(\tau)\, d\tau = 1$,

3. ω and τ are real and span from 0 to ∞.

The semicircle in the Cole-Cole diagram in the complex modulus form, is

$$\left| \epsilon^* - \epsilon_\infty - \frac{\epsilon_0 - \epsilon_\infty}{\epsilon} \right| = \frac{\epsilon_0 - \epsilon_\infty}{2}. \tag{2}$$

From Eq. (1), therefore,

$$\left| \int_0^\infty \frac{g(\tau)}{1 + i\omega\tau}\, d\tau + \frac{1}{2} \right| = \frac{1}{2}. \tag{3}$$

After a rationalization,

$$1 = \iint \frac{1}{2} \left[\frac{1 - \omega^2 \tau_1^2 - 2i\,\omega\tau_1}{1 + \omega^2 \tau_1^2} \cdot \frac{1 - \omega^2 \tau_2^2 + 2i\,\omega\tau_2}{1 + \omega^2 \tau_2^2} \right.$$

$$\left. + \text{complex conjugate} \right] g(\tau_1)\, g(\tau_2)\, d\tau_1\, d\tau_2$$

$$= \left[\int \frac{1 - \omega^2 \tau^2}{1 + \omega^2 \tau^2}\, g(\tau)\, d\tau \right]^2 + \left[\int \frac{2\,\omega\tau}{1 + \omega^2 \tau^2}\, g(\tau)\, d\tau \right]^2$$

$$= M^2 + N^2, \tag{4}$$

with M referring to the first bracket and N to the second bracket. They are functions of ω.

We observe the following properties of M:

1. $M(o) = 1$, $M(\infty) = -1$. This is based on the property 2 of $g(\tau)$,

2. M is a monotonically decreasing function of ω. This is proved by showing that for two values of ω, ω_1 and ω_2,

$$M(\omega_2) - M(\omega_1) = 2\,(\omega_1^2 - \omega_2^2) \int \frac{g(\tau)}{(1 + \omega_1^2 \tau^2)\,(1 + \omega_2^2 \tau^2)}\, d\tau \tag{5}$$

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Since the integrand is positive definite

$$M(\omega_2) - M(\omega_1) < 0 \quad \text{if} \quad \omega_2 > \omega_1 \tag{6}$$

From these properties of M, we conclude that M has once and only once a value zero at some frequency, say, ω_0.

Now, trivially, $g(\tau)$ cannot be zero everywhere. If $g(\tau)$ is non-vanishing at an arbitrary interval of τ, with $\tau_1 < \tau < \tau_2$, then,

$$1 - N = \int_{\tau_1}^{\tau_2} \frac{(1 - \omega\tau)^2}{1 + \omega^2 \tau^2} \, g(\tau) \, d\tau > 0, \tag{7}$$

because $(1 - \omega\tau)^2/(1 + \omega^2\tau^2) \geq 0$. Therefore, $N < 1$, irrespective of the values of ω. Now, at ω_0, the condition given by Eq. (4) clearly cannot be satisfied. Therefore, $g(\tau)$ cannot be non-vanishing at any interval. Therefore, $g(\tau)$ can be non-vanishing only at singular points. This constitutes the proof of $g(\tau)$ as a δ-function.

Substituting the above result, by writing

$$g(\tau) = \delta(\tau - \tau_0), \tag{8}$$

into Eq. (1), we then obtain the familiar Debye relaxation function,

$$\epsilon^* = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{1 + i\omega\tau_0}. \tag{9}$$

This completes our proof.

III. DISTRIBUTION FUNCTION OF RELAXATION TIMES

In this part, we will discuss a method to identify two types of distribution functions. The mathematical basis of the method is very simple and is contained implicitly in the discussion of Part II. However, in order to attain an analytical

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completeness, we make here a formal elaboration of these distribution functions. These two types do not include all possible mathematical distribution functions, nor all dispersion functions one encounters in the experiment, but they include probably all the mathematical form of distribution functions discussed in the physical literature on relaxation.

In the first type, $g(\tau)$ is zero everywhere except at one value of $\tau = \tau_0$, and has the property

$$\int_0^\infty f(\tau)\ g(\tau - \tau)\ d\tau = f(\tau_0), \tag{10}$$

that is, $g(\tau)$ is a Dirac δ-function. This type of $g(\tau)$ has already been discussed in Part II.

In the second type, $g(\tau)$ is a continuous, unimodal distribution function of τ. By unimodal we mean that $g(\tau)$ has one and only one maximum.[9] This type of $g(\tau)$ is represented by a vast number of dispersion functions in the literature, for example, Cole and Cole relaxation in dielectrics[11] and Weichert relaxation in viscoelasticity.[10]

Sometimes in mathematical statistics, a null-function type of distribution can be found. This function is non-zero only at some discrete points of τ, and the integration of such a $g(\tau)$, as indicated in Eq. (10), is zero. We are not aware of the physical application of such a function in the relaxation dispersion, and will not discuss it.

It is possible to have physical systems where $g(\tau)$ is a linear combination of functions of the two types we stated in the beginning. A very particular case would be that all τ_0 has the same value. In this case, if $g(\tau)$ consists of a combination of pure first type or pure second type of distribution, one can not distinguish such a resultant distribution function from a single first or second type of distribution function respectively. An interesting case is that of $g(\tau)$ consisting of a linear combination of mixed types of distribution functions, all with same τ_0. Such a function, to our knowledge, has been discussed only in quantum field theory,[11] but not in other branches of physics, and we will not make any further discussions.

It remains for us to discuss the case of distribution function which is a linear combination of the two types of distribution function, each component of which has a value of τ_0 different from all other τ_0. In principle, then one can separate the corresponding dispersion function into single components for each distribution function.[12] After the problem of separation is solved, the results which will be given here can be applied to each component.

Now we will discuss a method to identify the two types of specific distribution functions from the dispersion data derived from the frequency domain. In an investigation of the characteristics of dispersion in the frequency domain, the straightforward process is to represent the dispersion quantities in their frequency spectra. But the shape of the spectra usually cannot be described in terms of some simple geometrical form as to provide a direct identification without an elaborate analysis. On the otherhand, we found that Cole-Cole diagram provide a convenient means to identify different types of $g(\tau)$. This is based on the following consideration:

Always with the restriction of the special types of distribution function as specified in the beginning of this Part, from the result of Part II, we have proved that an Argand diagram of $\epsilon^*(\omega)$ is a semi-circle with the center at the real axis if and only if $g(\tau)$ is a δ-function. Therefore, if the Argand diagram is not a semi-circle, $g(\tau)$ is a continuous distribution function.

CONCLUSION

In this paper, we proved that a semi-circle in the Cole-Cole diagram implies uniquely the relaxation function is that of Debye. Although the inverse statement was well known, as it can be proved readily by a simple algebraic method, the proof of the present problem requires some novel procedures as it has to deal with a non-analytic, singular function.

As a corollary, the above result is used to establish the criterion of recognizing a continuous distribution of relaxation times.

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